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Para-excitons in Cu_2O—a new approach

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Abstract

We propose a non-resonant two-photon absorption as a method to create a high-density gas of para-excitons uniformly distributed in a whole volume of a crystal. In non-linear pump–probe experiments we measure changes of the IR absorption induced by the presence of optically excited para-excitons. This way, we directly determine the energy of the para-excitonic $1s \rightarrow 2p$ transition at 129 meV. On the basis of temporal evolution of the induced absorption signal we find the lifetime of the para-excitons to be of the order of 10 ms.

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Keywords: Intra-band transitions; Para-excitons; Ir transmission

1. Introduction

Cuprous oxide (Cu_2O) is a long-recognized excitonic system. Recent revival of interest in this system is related to the fact that Cu_2O seems to be a very good candidate for observation of Bose–Einstein condensation of excitons. In Cu_2O one can distinguish up to four excitonic series attributed to various combinations of valence (V) band holes and conduction (C) band electrons. The energy range explored in our experiments allows us to take into account only two series span between the uppermost valence band and two conduction bands (see also the schematic band structure depicted in Fig. 1). The series are known as yellow ($V_1 - C_1$) and blue ($V_1 - C_2$) excitons. The excitonic ground state, 1s yellow exciton, is split by the exchange interaction between an electron and a hole into a 1s-ortho state ($J = 1$) at 2.034 eV and a 1s-para state ($J = 0$) laying 12 meV below at 2.022 eV. Both the conduction band (C_1) and the valence band (V_1) have a positive parity. Hence, dipole transitions over the direct gap ($E_g = 2.17$ eV at 10 K) at the center of

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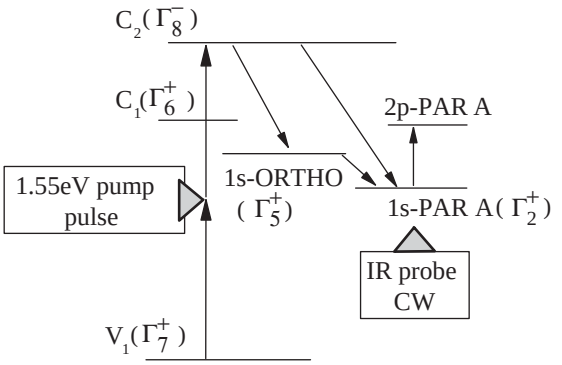

Fig. 1. Two photon excitation diagram.

a Brillouin zone are parity forbidden. As a consequence of the symmetry constrains radiative decay of ortho-excitons is only quadrupole allowed while for para-excitons is forbidden in any order. This results in an exceptionally long, defect limited, lifetime. Moreover, excitonic binding energy at a ground state is as high as 150 meV which leads to a Bohr radius of about 7 Å. In such a case excitonic gas of a very high density ($n \approx 10^{20}\,cm^{-3}$) may still be considered as a non or weakly interacting gas [1]. The long life of excitons is a prerequisite to have a chance to observe Bose–Einstein condensation of excitons. Thus we need a system in which a particle loss rate is much slower than the cooling rate. Ortho-excitons in Cu_2O do not fulfill this condition [2].

For all these reasons attention got focused on para-excitons in Cu_2O which appear to be the best candidates for Bose–Einstein condensation in bulk systems.

The first experimental attempt to measure Lyman transitions within yellow excitonic series was made by Göppert et al. [3]. However, they did not succeed in observing a signal that might be attributed to the para-excitons. Only recently, the two groups reported to observe the aforementioned transition at the energy ≈ 129 meV [4,5]. Our results confirm the previous reports. On top of that we also make an estimate for a lifetime of the para-excitons at the ground state and we find it to be as long as 10 ms.

2. Experimental details

The sample used in this study was a [1 0 0] platelet 0.7 mm thick cut from a high-purity Cu_2O single crystal grown by a floating zone technique [6]. The sample was polished and mounted on a cold finger of a continuous flow cryostat and kept at $T = 4$ K. Pump-pulse, 120 fs long, of energy $E_P = 1.55$ eV was produced using an amplified Ti–sapphire laser system. The excitation pulse was slightly focused on the sample with a spot size of about 2 mm. The transmission was measured using Bomem interferometer equipped with an MCT detector. The population of the ground state of para-excitons was probed by a broad-band CW IR-source which covered an energy range within which a para-excitonic 1s–2p interband transition was expected.

Detailed studies of the applied excitation method were reported elsewhere [2]. The excitation diagram is presented in Fig. 1. A two-photon absorption to the second conduction band C_2 serves as an intermediate step in the excitation process. Eventually the excitation leads to the creation of yellow para-excitons either directly or via fast-decay of the 1s ortho-excitons (at $T = 4$ K a down-conversion time of the order of 1.5 ns is commonly observed [2]). From the group symmetry point of view one would not expect an efficient two-photon transition between bands of different parities, as it is in case of V_1 (Γ_7^+) and C_2 (Γ_8^-) bands. However, as it was shown by Mahan [7] in the case of allowed dipole transition, the two photon absorption also takes place but to the excitonic states of a p-type envelope function. The detailed studies of the excitation spectrum reported in Ref. [2] strongly support the conclusion that the two-photon transition takes place to the p-state continuum of blue excitons.

The exact nature of the process responsible for the energy transfer from blue to yellow excitons is not yet clear and requires further investigation. However one thing is clear, there is no dipole coupling between p-type excitonic states in blue series and s-type states of a yellow series. To fulfill symmetry conditions either there must take place an additional emission (absorption) of a phonon

or an extra optical transition within blue or yellow series.

As a result of the applied excitation method we achieve a high-density gas of yellow excitons at a ground state, uniformly distributed in whole volume of the crystal.

3. Results and discussion

In the case of yellow ortho-excitons the energy gap between ground (1s) and first excited (2p) states is well known to be 116 meV [8]. For extended 2p states one expects an exchange interaction to play only a minor role so both ortho and para 2p states should lay very close to each other. Therefore $1s(\Gamma_2^+) \rightarrow 2p(\Gamma_5^-)$ transition for para-excitons should take place at the energy 12 meV higher than for ortho-excitons namely at ≈ 128 meV. To verify that we measured pump laser-induced change of the transmission (T) of the sample in the corresponding infrared region. The transmission spectrum measured without pump beam at $T = 10$ K is presented in Fig. 2. The strong absorption band at approx. 140 meV is attributed to the absorption of the two transverse optical phonons [9]. The band is strongly temperature dependent, both in position and shape. Since the band belongs to a background signal, which has to be properly subtracted at the end, it is important to keep the density of the excitation power low enough to avoid heating of the sample during measurement. Hence only a weak focusing of the pumping beam is chosen for our experiment.

The relative change of the transmission in the vicinity of the predicted 1s–2p para-excitonic transition is presented in Fig. 3. The presence of excitons is expected to cause an additional absorption, manifested as a decrease of the intensity of the transmitted probe beam. Indeed, in the transmission spectrum we observe a sharp dip at 129.3 meV with a full-width at half-maximum (FWHM) $\Gamma = 0.25$ meV. The position of the dip is in very good agreement with the energy predicted for $1s \rightarrow 2p$ para transition. It also agrees with the transition energy recently reported in Ref. [4]. In Fig. 3 the two data sets are obtained for two average excitation powers, namely, 4 mW that corresponds to energy of 4 μJ/pulse and 16 mW corresponding to 16 μJ/pulse. For the energy of $P = 4$ μJ/pulse and higher we did not observe any power dependence of neither the position of the dip nor its depth in spite of the fact that we still see an increase of the population (intensity of the emission) of ortho-excitons [2]. Since para-excitons are also formed due to down-conversion of the ortho-excitons this discrepancy cannot be

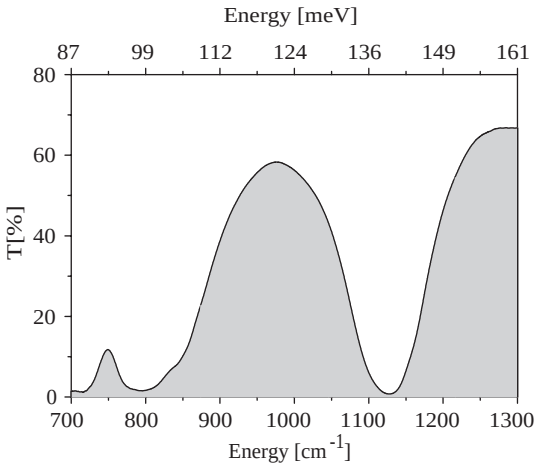

Fig. 2. Infrared transmission spectrum measured at $T = 4$ K without laser pumping.

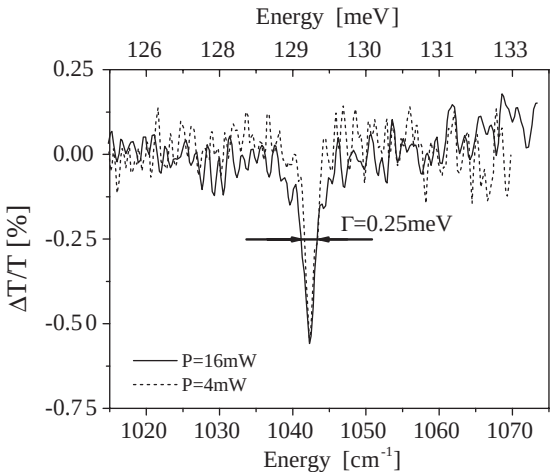

Fig. 3. Laser-induced change of the transmission measured at $T = 4$ K for given average excitation powers.

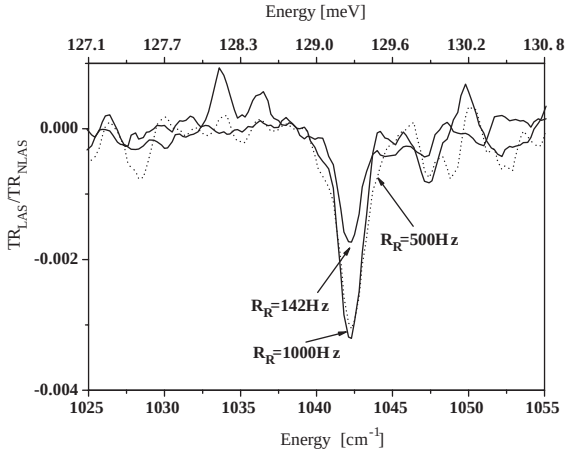

Fig. 4. Laser-induced change of the transmission measured at $T = 4\,\mathrm{K}$ for given pump-beam repetition rates.

explained by saturation of the pumping efficiency. It is likely to be caused by a saturation of the population of para-excitons at the ground state due to their long lifetime. The repetition rate of the pump-laser in use was only 1 kHz, so it would mean that we deal with an exciton lifetime (τ_P) of the order of millisecond. That long lifetime, exactly $\tau_P = 3\,\mathrm{ms}$ was in fact predicted by Jolk et al. [10] on a basis of numerical modeling of the transport measurements. Jolk et al. in fact made the first attempt to estimate the τ_P in an unperturbed system, namely, without any strain applied to the sample to form a potential trap for excitons. The strain lifts the symmetry constrains for the para-excitonic emission and makes it weakly allowed but simultaneously shortens the lifetime of excitons by orders of magnitude. In the presence of a potential trap τ_P of an order of microsecond was reported [11].

To verify our approximation we used even slower pump repetition rate (R_R). The results obtained for R_R equal to 1000, 500 and 142 Hz respectively are collected in Fig. 4. For 2 ms between pump pulses, the signal remains almost as strong as for 1 ms. Only for the time between pulses as long as 7 ms the intensity of the excitonic absorption decreases significantly. It would not be the case if τ_P would be of the order of 3 ms as proposed in Ref. [10], it must be significantly longer. For the induced absorption to show the observed R_R dependence, τ_P must be of the order of 10 ms or even longer. A more accurate value of τ_P requires more detailed studies of the induced absorption dependence on the R_R of the pulse beam. At this stage however, we can already conclude that indeed para-excitons in a strain-free sample have an exceptionally long lifetime at low temperatures.

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